Nitrogen Chemistry in an Urban Bioretention System in Singapore

By
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Abstract

An investigation into the nitrogen chemistry of the anoxic layer of an urban constructed wetland in Singapore was conducted. This pilot-scale wetland treats stormwater runoff from the Balam Estate housing development for several water quality parameters of concern, including nitrate. Earlier sampling in the wetland had indicated that the concentration of nitrate was lower in the outflow from the rain garden than in its inflow, but no research had been done on other nitrogen species or transformation pathways.

Preliminary analyses suggest that, although the saturated layer is sufficiently anoxic and denitrification is occurring as per performance objectives, organic nitrogen is being added to the infiltrating water throughout this layer, causing a net export of total nitrogen from the anoxic zone. This organic nitrogen could be either re-released from reserves adsorbed onto organic material during previous storm events, or leached directly from the anoxic layer material which includes wood chips and sand. Readings at outflow pipes indicate that a percentage of this nitrogen is likely re-mineralizing to ammonia upon exposure to more oxygen-rich conditions in the outflow pipes. Further study in the Balam Rain Garden using isotope labeling to more clearly delineate nitrogen fate and transport is suggested.

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1. Introduction

1.1 Water Management in Singapore

The following two sections were written in collaboration with Margaret Hoff, Ndeye Awa Diagne, and Tsung Hwa Sophia Burkhart in the MIT Civil and Environmental Engineering Department.

Many international bodies, including the World Health Organization, laud Singapore as an archetype of an integrated water resources management model (Chen et al. 2011). This recognition comes not because the small city-state has abundant water; on the contrary, it lacks sufficient naturally occurring water resources to sustain its population of 4.8 million. Water limitations are serious enough to warrant Singapore's inclusion by the United Nations on its list of water-scarce countries (Ong 2010). Though the average annual rainfall of 2,500 mm is above the global average, the country lacks the land area necessary to harvest an adequate amount of that precipitation (Chen et al. 2011). Furthermore, the small island has no other sources of renewable fresh water, as it lacks the reservoirs of surface- and groundwater that typically sustain other countries. Singapore, which consumed approximately 1.36 billion liters of water per day as of 2006 (Tortajada 2006), is projected to reach a population of 6.5 million in the next 50 years (Chen et al. 2011), further stressing its already scarce water resources.

Singapore scores remarkably high on a measure of the proportion of the population with adequate water supply, both in terms of quantity and quality. As Chen et al. (2011) report, 100% of the population has consistent access to water of sufficient quantity to meet their consumption demands. Furthermore, 99.96% or higher of that water supply meets the World Health Organization (WHO) drinking water standard, which, though not a universal standard, is generally considered sufficient to ensure water potability. Similarly, 100% of the population is reported to have access to "adequate sanitation" (Chen et al. 2011). Singapore's national water utility, the Public Utilities Board (PUB), carefully manages the country's four major sources of water, designated the four "National Taps." This deliberate conservation results in the country's impressive performance despite its water scarcity (Chen et al. 2011).

As mentioned above, Singapore receives an above-average amount of rainfall but is simply not physically large enough to collect and retain enough rainfall. This spatial limitation has long been the target of engineering projects in Singapore and has resulted in an intricate network of

rainwater collection channels and reservoirs, considered the country's first National Tap (Chen et al. 2011). The rainwater collection system provides about 50% (Chen et al. 2011) of Singapore's daily water consumption of 1.36 billion liters (Tortajada 2006). Efforts to expand the ability to harvest precipitation are continuing, including progressive rooftop harvesting schemes and continuous expansion of the reservoir network, with the aim of transforming 90% of Singapore's land area into water catchment. Despite the advanced technology and the government's aggressive expansion of rainwater collection systems, physical limitations still necessitate other sources of water to meet the country's needs (Chen et al. 2011).

Singapore's second National Tap is imported water from Johor, Malaysia, which comprises another 40% of its water supply (Chen et al. 2011). Singapore has imported a large percentage of its water since separating from Malaysia in 1965, but in intervening years the relationship has often been tense and uncertain. At various times, Malaysia has threatened to cut off the water supply for political or economic reasons, and agreement on pricing has been a long-standing issue (Chen et al. 2011). An agreement currently exists that will provide water to Singapore through 2061 at a price of less than S$0.01 per 1,000 liters, but further terms are undefined (Tortajada 2006). Driven by at-times acrimonious relations with Malaysia, Singapore has investigated other international sources for water, including Indonesia, but has been deterred by high development costs and the inherent insecurity of relying on other nations for natural resources (Chen et al. 2011). Most recently, Singapore has invested significant financial and political resources into careful water resource management and development of its third and fourth National Taps (desalination of seawater and reuse of wastewater) with the ultimate goal of national water independence (Tortajada 2006).

The country's first large desalination plant, the Tuas Desalination Plant, opened in 2005 with a price tag of S$200 million (Chen et al. 2011). Though desalination technology is improving rapidly, it still has relatively low capacity and high energy demand. Accordingly, the Tuas plant can supply 113 million liters per day (less than 7% of the country's current water demand) at a cost of S$0.78 per 1,000 liters (Tortajada 2006). For a sense of scale, this water source is more than seventy times more expensive than imported water, but, as of 2011, was still the lowest cost seawater desalination plant in the world (Chen et al. 2011). High costs and lagging technology in

desalination have encouraged Singapore to explore water reuse technologies, which typically have lower economic costs than desalination but higher social barriers.

Singapore has explored reuse of highly treated wastewater as an alternative water source since 1972, with the first operational treatment plant built in 2000 (Tortajada 2006). The recycled waste stream and fourth National Tap, locally termed "NEWater," is currently produced at four facilities across the country and will ultimately account for more than 30% of the national water supply (Chen et al. 2011). Though treated to a higher level than necessary to meet standards for human consumption, the majority of NEWater is currently used for industrial water needs rather than domestic (potable) distribution. Since 2003, a small percentage of the recycled water has been designated for indirect potable use, through which the highly treated effluent is mixed into existing raw water sources (Ching 2010). The percentage of NEWater designated for indirect potable use is expected to rise but will still remain much lower than industrial usages (Tortajada 2006). As with desalination, production costs will likely drop as technology evolves, but current reuse treatment costs are already approximately S$0.30 per 1,000 liters: less than half the cost of desalination (Tortajada 2006).

Singapore's success in water provision, particularly in the arena of water reuse, has been attributed largely to the organization of its formal water management institution, the Public Utilities Board. Since 2001, PUB has managed the entire water cycle within the country, including potable water delivery, sewage, waste treatment, and rainwater collection (Chen et al. 2011). In addition to controlling the entire water cycle, PUB was also given general autonomy over its functions. This has allowed the agency unilateral authority over all aspects of water governance, including pricing structures, regulatory frameworks, and enforcement mechanisms (Tortajada 2006). This structure is believed to "eliminate administrative barriers in water management and make implementation effective and efficient" (Chen et al. 2011). Furthermore, PUB is widely considered to effectively include the private sector when appropriate and foster public acceptance and political will through its success (Tortajada 2006).

1.2 Water Quality Concerns in Singapore

In 2006, PUB launched the Active Beautiful Clean Waters (ABC Waters) Programme, a strategic initiative to open Singapore's reservoirs and waterways to the public for recreational activities.

The larger objectives of the ABC Waters Programme are to encourage Singaporeans to cherish their water bodies, and to raise public awareness of water scarcity (PUB 2009). Recreational activities in question include kayaking, fishing, barbecue, and picnic activities, and may involve direct contact with the water bodies. However, water quality of the reservoirs and waterways has been a concern for PUB. Recent studies have reported contamination in the reservoirs and associated stormwater drains. Urban runoff has been reported to contain high levels of pollutants including suspended solids, nutrients, heavy metals, and pathogenic bacteria (Wang 2012). Furthermore, nutrient discharge to waterways is a major cause of eutrophication. In order to protect public and environmental health, PUB has funded ongoing studies to evaluate the levels of contamination within reservoir catchments and bacteria loading to the reservoirs, as well as best management practices (BMPs) for reducing pollutant loads to waterways in an efficient and eco-friendly manner (Chua et al. 2010).

1.3 Bioretention Systems

A bioretention system, or rain garden, is a relatively low-cost, low-maintenance best BMP harnessing natural processes in soil and vegetation to remove pollutants from stormwater runoff (Roy-Poirier et al. 2010). Several studies have shown that urban stormwater runoff is a significant contributor to pollutant load, specifically nitrate (Kim et al. 2003). In addition to the aforementioned practical benefits, a rain garden has the advantage of keeping the existing hydrology of the area intact by treating close to the source of the runoff, thereby fulfilling the requirements of a low impact development (LID) design. Designs of rain gardens can vary widely, based on local climate, hydrology, treatment needs, and regulations. These bioretention systems have the capability to remove suspended solids and metals largely via physical mechanisms, such as sedimentation and filtration. However, nutrient removal is biologically mediated and more complex (Palmer 2012).

1.4 Balam Rain Garden Purpose and Design

The Balam Estate Rain Garden is Singapore's first bioretention system (Figure 1) (Ong et al. 2010). The garden was designed as a pilot project of one of several best management practices chosen by PUB for the treatment of non-point source pollution (Wang 2012). The garden is 240 square meters of active treatment area, covered in vegetation, and treats a residential area of

approximately 6000 square meters. The garden is divided approximately in half by a bicycle path, with the smaller southwest section draining into the larger northeast section. Treated runoff is released from the northeast section to the Marina Reservoir by way of the Pelton Canal (Wang 2012).

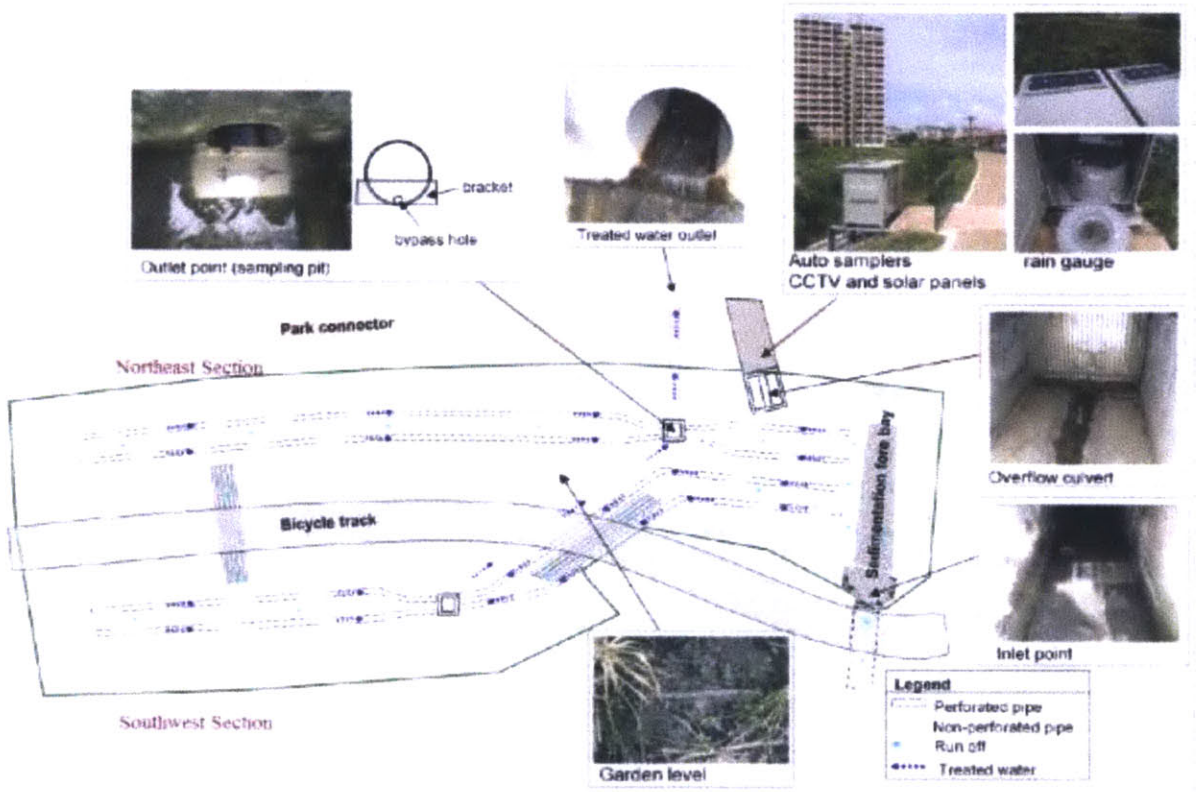

Figure 1: Balam Rain Garden schematic (Ong et al. 2010)

Key treatment parameters of interest for the Balam Rain Garden are total suspended solids, nitrogen, and phosphorous removal. The garden is designed in vertical layers, including a vegetation layer, an extended-detention level, a sandy-loam filter media, a coarse-sand transition layer, a rock and wood chip saturated anoxic zone, and a fine-gravel drainage layer. A U-shaped drainage pipe runs underneath the garden, as seen in Figure 2, whose shape creates the saturated anoxic zone by only allowing outflow 40 cm above the bottom of the garden's subsurface layers.

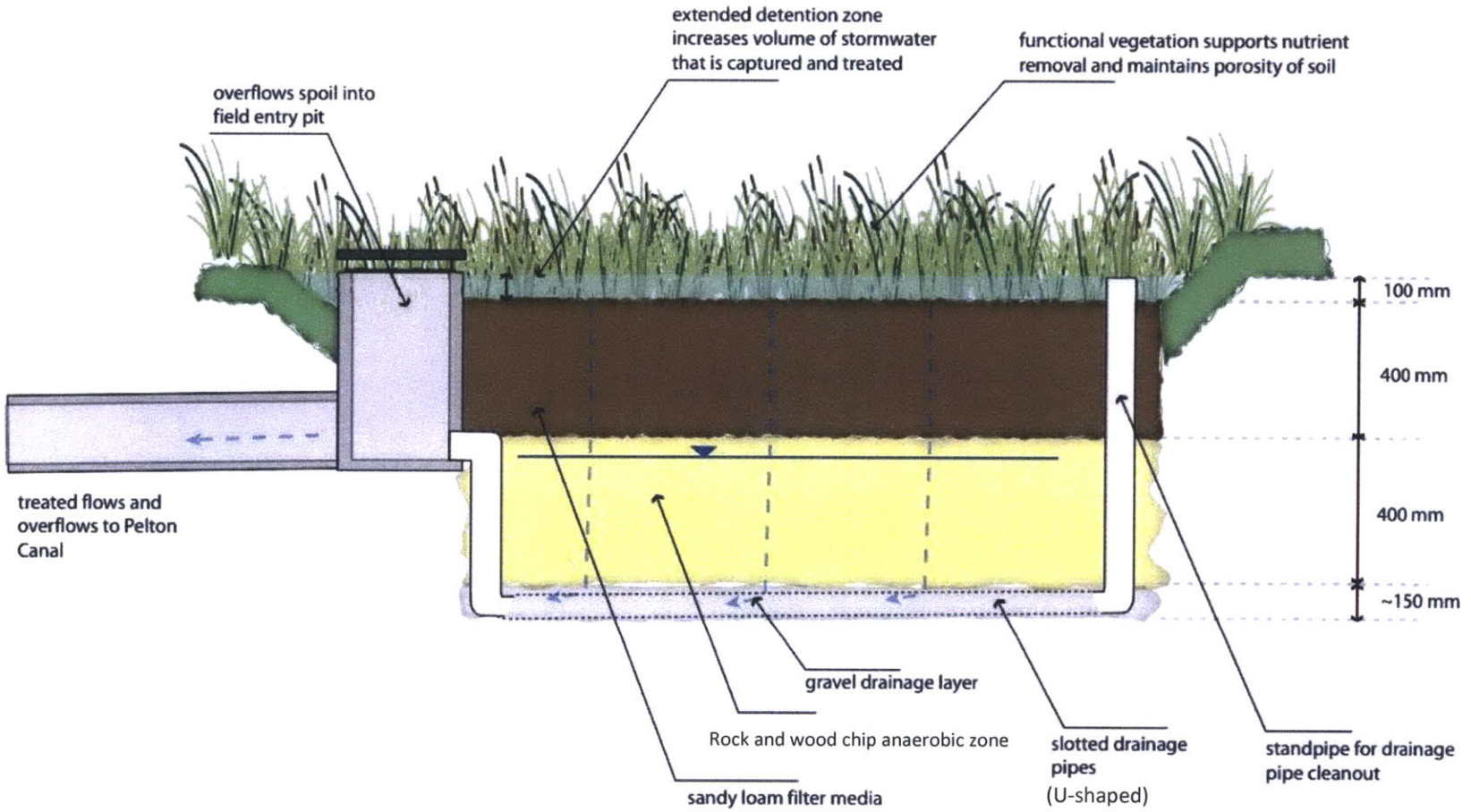

Figure 2: Balam Rain Garden cross section. Coarse sand transition layer occurs between sandy loam filter media and rock and wood chip saturated anaerobic zone (Wang et al. 2009).

The saturated anoxic zone facilitates denitrification of the stormwater runoff, fueling the nitrogen removal capability of the garden. Denitrification reduces nitrogen species and in its complete series reduces NO_3^- and NO_2^- to N_2 gas. This reaction requires an electron donor and carbon substrate. The classical full reaction is as follows:

$$\frac{1}{5}NO_3^- + \frac{1}{4}CH_2O + \frac{1}{5}H^+ \rightarrow \frac{1}{10}N_2 + \frac{1}{4}CO_2 + \frac{7}{20}H_2O \quad (1)$$

where CH_2O represents a generic organic carbon source undergoing biodegradation. In the rain garden, the wood chips in the saturated anoxic zone serve as the carbon substrate and electron donor.

2. Literature Review

2.1 Denitrification Rates in Bioretention Systems

A multitude of studies attest to the potential efficacy of bioretention systems for denitrification; however, design parameters of the system greatly impact its performance. Greenan et al. (2006), in an ex-situ study measuring the relative denitrification rates of various carbon substrates, report a nitrogen removal rate of 80% using a substrate of wood chips sized 3 to 10 centimeters, with the removal rate remaining steady over the course of 180 days. In a similarly-designed study, Saliling et al. (2007) found a nitrogen removal rate of up to 99% for wood chips of size 0.8 to 5 cm, with influent concentration as the only limiting factor. Kim et al. (2003) report a maximum nitrogen removal rate for pulverized wood chips (<2 mm) of 95%, although this value may be less comparable due to the dramatically different size and surface area of the substrate particles. Two in-situ studies of septic system nitrate removal found removal rates varying from 58% to 98% at influent concentrations ranging from 4.8 mg/L to 57 mg/L of nitrate (Robertson et al. 2000; Robertson et al. 2005). However, Bratieres et al. (2008) found a net export rate of 158% for a 20% plant-based organic medium at nitrate loading rates of 0.79-1.40 mg/L. Several other studies also find net export rates under varying conditions (Palmer 2012).

One major factor affecting denitrification rates is the chemical composition of the substrate. In the Balam Estates Rain Garden, the substrate is wood chip. Wood is theoretically 45-50% carbon, 40-50% oxygen, 6% hydrogen, and <1% nitrogen (Chandrasekaran et al. 2012). Greenan et al. (2006) report the initial C-to-N ratio of hardwood chip in their denitrification rate study at approximately 450. Saliling et al. (2007) report a similar value of 390.

Denitrification rates can be inferred from in situ measurements of nitrate concentration data coupled with distances and hydraulic retention times. This method assumes that denitrification is the primary pathway for nitrate removal in the system. Nitrate concentrations can be measured in the field using spectrophotometric field kits at an accuracy commensurate with laboratory spectrophotometer measurements (Ormaza-Gonzales and Villalba-Flor 1994).

Studies on vertical denitrification profiles in systems with high denitrification capacity find that the highest rates of denitrification occur near the inflow of the system and decrease moving

downwards through the column of rain garden media. Saliling et al. (2007) found that about 60-70% of nitrate removal occurred in the first 10 cm of a 40-cm laboratory column. This supports the conclusion that the system has more denitrification capacity than is utilized by influent nitrate concentrations.

2.2 Substrate Mass Loss

Substrate mass loss is a concern in bioretention systems because degradation of substrate determines the useful lifespan of the system.

Several metrics can be utilized to investigate substrate mass loss. Several studies use assumptions regarding the primary mass-removal mechanisms, the most common being that denitrification dominates degradation through carbon removal. With these assumptions, mass loss can be inferred from mechanistic rates. Another quantitative indicator of mass loss is decreasing C-to-N ratio. Finally, decreased porosity, darker color, and increasing chip breakage can all be qualitative indicators of substrate degradation (Saliling et al. 2007).

In a study of in-situ reactive barriers for septic systems, Robertson et al. (2000) tested field sites with barriers containing 15-100% cellulose by volume and found that only 2-3% of the initial carbon mass was lost over a period of six years, assuming denitrification as the major removal mechanism. In a later in-situ study of Nitrex filters (containing ground wood byproduct with high C-to-N ratio) with the same mechanistic assumption, Robertson et al. (2005) calculated mass balances that indicated that these filters contain enough carbon substrate for at least five years of operation under influent nitrate concentrations of between 14 and 38 mg/L. Based on their 140-day in-situ study, Saliling et al. (2007) estimate a mass loss of 16.2 ± 5.2%, corresponding to a 42% reduction rate over a year assuming a linear rate of change and denitrification as the primary removal mechanism. C-to-N ratios at the end of the study were found to have decreased from around 390 to 190. No losses in bed height or structural issues were observed in this time period. The authors assume the end of useful substrate lifespan to be >50% mass loss (although no references or data are provided to support this number) and therefore estimate the useful lifespan of wood chip substrate for denitrification to be approximately 1 year. Kim et al. (2003) did not test mass removal rates of wood chips, but

estimated an approximate lifespan for newspaper substrate of 20 years. It is unclear whether this value is based on a >50% mass loss assumption similar to Saliling et al. (2007).

2.3 Competing Processes

Denitrification is not the only nitrogen-related process occurring in natural or constructed saturated areas. Dissimilatory nitrate reduction to ammonia (DNRA) can also occur under similar anoxic conditions. This process is undesirable in bioretention systems, as the nitrogen remains bioavailable in the form of ammonia. A pattern of decreasing nitrate coupled with simultaneous increase in ammonia under anoxic conditions can be suggestive of DNRA. Several sources note that DNRA is more likely to occur when the available organic material has a high C-to-N ratio (Kim et al. 2003; Rutting et al. 2011). Rutting et al. (2011) state that "under NO_3^- limiting and strongly reducing conditions [...] DNRA has the advantage over denitrification since more electrons can be transferred per mole NO_3^-." Kim et al. (2003) hypothesize that DNRA may be responsible for the high total Kjeldahl nitrogen (TKN) effluent values in their study. Greenan et al. (2006) observed ammonium production under all of their test conditions, but this production was low compared with overall nitrogen removal rates.

Furthermore, leaching of organic material can complicate the conceptual model of nitrogen removal. Both organic nitrogen and carbon can leach from rain garden media, and can come either from embodied nitrogen and carbon in substrate material or organics adsorbed onto substrate material from previous storm events (Palmer 2012). Palmer's 2012 dissertation on nitrate and orthophosphate removal in bioremediation systems used a soil mix including 15% compost and 15% shredded cedar bark in test columns, and found that organic nitrogen was being leached under every set of experimental conditions. The author confirmed this result in separate leaching tests of the soil mix. On average, the compost in the study leached "up to roughly 14 mg/L (per 20 grams of material in 1 liter of water)." However, the author found that leaching rates decreased with increasing age of soil material in the test columns, likely indicating leaching primarily from embodied material rather than adsorbed nitrogen. In the Nitrex filter study, Robertson et al. (2005) note that soluble organics often leach for several months after installation. However, they also report that this leaching is a low percentage of the overall mass of the wood, and that the leaching subsides with time. The earlier Robertson et al. (2000) study addresses leaching of organic carbon when discussing mass calculation and data from several of

their test sites suggest some carbon leaching. However, they argue that in the case of a septic system, excess dissolved organic carbon (DOC) will be mitigated by oxidation at later steps in the system. Kim et al. (2003) note generally that if the carbon substrate decomposition rate is excessive for the amount of introduced nitrogen, high total organic carbon (TOC) and TKN in effluent water may result.

2.4 Balam Rain Garden Performance Monitoring

In a report for the Public Utilities Board of Singapore, Ong et al. (2012) outlined the results of performance monitoring in the Balam Rain Garden. For an average of six rainfall events, inflow and outflow total nitrogen (TN) were 1.21 mg/L and 0.66 mg/L, respectively, indicating a 46% reduction through the rain garden. The authors note that these influent values are relatively low compared to global averages and are reduced to approximate background concentrations, explaining the apparently low percent removal. A portion of the stormwater flowing into the garden is retained and/or infiltrated, such that total outflow is less than total inflow. Taking these retention and filtrate volumes into consideration, the inflow and outflow concentrations correspond to TN loads of 0.070 and 0.023 kg per rain storm, respectively, for a 64% reduction. Loss in water volume is attributed to uptake by plants, soil media wetting, and storage in the saturated layer. The authors calculate the garden detention time as 6-10 hours, which is on a comparable scale to the design detention time of 6-8 hours. They also note that the volume of water passing through the garden during a storm often exceeds detention capacity, so the garden overflows and some of the water is diverted through the overflow drains directly into Pelton Canal without treatment. According to Ong et al. (2012), the limiting design factors for detention volume were safety considerations rather than optimal hydrologic performance, leading to the frequent overflows.

3. Procedure

3.1 Soil Sampling Procedure

Soil samples were collected at eight locations around the rain garden, of which five were located in the larger northeast section. Sample locations were recorded by GPS. At each location, a 42-inch 1.25-inch-diameter Oakfield Model S stainless steel soil auger (Ben Meadows, Janesville, WI) was used to auger as far into the soil as possible before encountering unyielding material. Greater resistance at the transition to the anoxic layer was often palpable while augering. In at least one sample, a rock was hit before the deeper parts of the anoxic layer were reached. Upon reaching maximum possible depth, the auger was removed vertically from the hole, and the soil clinging to the threads was collected. The auger was then rinsed with clean, commercially bottled water before repeating the procedure at the next location. Some samples resulted in dark brown or black fibrous anoxic layer material being collected, often containing intact pieces of wood chip, while other samples collected mostly unsaturated or transition zone sandy material. Samples were placed on ice immediately after collection, and refrigerated at Nanyang Technological University (NTU) at approximately 5 degrees Celsius. The five samples which contained the largest quantity of anoxic layer material were transported back to the United States and frozen. The other three remained refrigerated in Singapore until subsequent use in a leaching experiment as described below.

3.2 Groundwater Sampling Procedure

Subsurface water samples were also collected within the rain garden. At each of four selected locations, a 3-mm steel rod was pushed into the soil to a depth of 65 cm and then removed. A Model PPX36 36-inch PushPoint ¼-inch-diameter Field Investigation Sampler (MHE Products, East Tawas, MI) was then placed in the hole created by the rod. This sampling well was connected to a portable-generator-powered peristaltic pump using clear silicone tubing. Water was drawn until clear, at which point temperature, oxidation-reduction potential (ORP), and pH readings were taken with a Myron 6Pfc Multimeter II (Myron L Company, Carlsbad, CA), calibrated approximately three days previously in accordance with manufacturer's instructions. Temperature readings were taken instantly; oxidation-reduction potential readings were allowed to equilibrate for approximately 30 seconds. pH readings were allowed to equilibrate for

approximately 60 seconds. After these readings were taken, approximately 750 mL of water from the well was collected into a glass bottle. Dissolved oxygen (DO) testing was done on-site using CHEMetrics Nos. K-7513 and K-7503 dissolved oxygen Rhodazine D kits (CHEMetrics, Inc., Midland, VA) and a CHEMetrics V-2000 Multi-Analyte Photometer in accordance with manufacturer's instructions, and the dissolved oxygen reading was recorded. The remainder of the water in the bottle was placed on ice in a cooler.

The PushPoint sampling well was then removed and rinsed thoroughly with clean water. The steel rod was replaced in the existing hole and pushed further to a depth of 75 cm, at which point the above procedure was repeated. A sample was then taken at a depth of 85 cm according to the same procedure. Samples were taken at a total of four sampling sites, each from depths of 65, 75, and 85 cm. Three of the four sites were in the larger, northeast side of the garden.

Coolers containing 250 mL of each sample on ice were transported to the laboratory at NTU and refrigerated for approximately 18 hours. At this point, tests for ammonia, nitrate, nitrite, total phosphorous, and chemical oxygen demand were performed with CHEMetrics kit Nos. K-1403, K-6913, K-7003, K-8540, and K-7361S, respectively, in accordance with manufacturer's instructions. Results were recorded.

For each sample, 500 mL were transported to Setsco Services Pte Ltd, who performed tests on total organic carbon as TOC (APHA test method Pt 5310B), total nitrogen as TN (APHA test method Pt 4500-N (C)), and total Kjeldahl nitrogen as TKN (APHA test method Pt 4500-N_{org} (D)). The results of these tests were delivered via email report.

3.3 Outflow Pipe Water Sampling Procedure

In each U-shaped outflow pipe, the intake tube of a plastic manual hand siphon pump was inserted into the pipe from field entry pit (Figure 2) such that the water sampled was taken from the bottom of the U. Water was pumped until as clear as possible, at which point the discharge tube from the pump was placed in a glass jar and approximately 750 mL of water were collected. Dissolved oxygen testing was done on-site using the aforementioned CHEMetrics dissolved oxygen kits and spectrophotometer in accordance with manufacturer's instructions, and the dissolved oxygen reading was recorded. The remainder of the water in the bottle was placed on

ice. A general note regarding whether the pipes were "actively weeping," "yielding plentiful water," or "yielding limited water" was also recorded.

Nine outflow pipes were sampled using the above procedure, five of which were in the northeast section of the garden.

3.4 Elemental Composition Analysis Procedure

An analysis for carbon, hydrogen, and nitrogen composition ("CHN analysis") was performed on the soil samples containing anoxic layer material. In this kind of analysis, the CHN analysis instrument combusts the sample, after which the carbon is trapped as CO_2, hydrogen is trapped as H_2O, and nitrogen passes through the traps as NO and is analyzed with a thermal conductivity detector. The quantity of these gases is then reported as a percent of the original sample mass. The particular instrument utilized in this compares calibration data with a cross-session running average so that data is comparable between sessions.

Soil samples were thawed and remaining sand was removed from the samples to the extent possible. Material from all samples was pooled due to the limited volume of anoxic material that could be collected. Two samples containing black, anoxic-layer "soil" was set aside for analysis. From the remainder of the pooled sample, several wood chips were extracted with forceps and shaved with a standard stainless steel straight razor blade to produce smaller-sized pieces for the analysis. Two samples containing shavings from the dark exterior of the chips were prepared, as well as two samples containing shavings from the lighter interior of the chips.

The CHN analysis was performed in two sessions. In each session, three instrument blanks with no sample or container were first performed, followed by conditioning with two samples containing acetanilide with a known CHN ratio. This was followed by three acetanilide samples used to calibrate the equipment. On the first day, this was followed by two anoxic "soil" samples and two samples of exterior wood chip material. On the second day, this was followed by two samples of interior wood chip material. Acetanilide samples were analyzed between every two to three experimental samples to ensure that instrument calibration remained accurate.

For each sample, the mass of an empty eight by five millimeter tin capsule was obtained by difference with another empty capsule of the same variety in a CAHN 25 automatic

electrobalance in the 20 mg range, read after 30 seconds. The tin capsule was then filled and the mass of the full capsule was obtained under the same conditions. The capsule was then pinched shut, folded to as small a size as possible, and placed in the Elementar vario EL III CHN analyzer. Instrumental settings were as follows: combustion furnace was set to 950 degrees C. Reduction furnace was set to 500 degrees C. The CO_2 column was set at a desorb value of 100 degrees C, and the H_20 column was set at a desorb value of 150 degrees C. The O_2 index was 90 seconds.

3.5 Leaching Test Procedure

The three anoxic layer samples remaining at NTU were combined and used for a nutrient leaching test. Approximately 1000 mL of milliQ water was poured into a glass sample container containing approximately 700 mL of anoxic-layer material. The container was capped, shaken, and left for eight hours with occasional shaking to re-suspend settled sediment. At the end of the eight-hour time period, the sample was left to settle for one hour, and 500 mL of water was siphoned from the top with a plastic hand syringe and silicon tubing into a clean 1000-mL glass container. The 500-mL sample of decanted water was sent to Setsco Services Pte Ltd. to test for TN (APHA method Pt 4500-N (C)), TKN (Pt 4500-N_{org} (D)), and TOC (Pt 5310B).

4. Results

4.1 Groundwater Analyses

4.1.1 Temperature, Dissolved Oxygen, pH, and Oxidation-Reduction Potential

Average parameter values as a function of depth are reproduced in Table 1. (See Appendices A and B for raw data tables.) Temperature readings remained essentially constant and independent of depth at approximately 28.5 degrees Celsius (Table 1). This value corresponds fairly well to the average yearly temperature in Singapore of approximately 27.5 degrees Celsius (NEA 2009). Dissolved oxygen values decreased by approximately 11%, from 1.75 to 1.55 mg/L, over the vertical profile (Table 1, Figure 3). Saturation DO at 28.5 degrees Celsius is approximately 7.7 mg/L (US EPA 2012), implying near-anaerobic conditions at the low concentrations measured. Dissolved oxygen values in the outflow pipes were 4.11 mg/L on average, but ranged between 2.11 and 7.01 mg/L. Outflow pipes observed to be dry consistently showed higher DO concentrations than those that were wet. pH increased by 10%, from 7.48 to 8.20, from top to bottom over the vertical profile. ORP exhibited the largest change over the vertical profile, changing by 120% from -88.8 to -193 mV. This change indicates increasing reduction potential with depth.

Table 1: Average parameter values as a function of depth

Depth from Surface (cm)	Temperature (°C)	pH	ORP (mV)	DO (mg/L)
65	28.6	7.48	-88.75	1.75
75	28.6	8.00	-151.50	1.72
85	28.5	8.20	-193.25	1.55

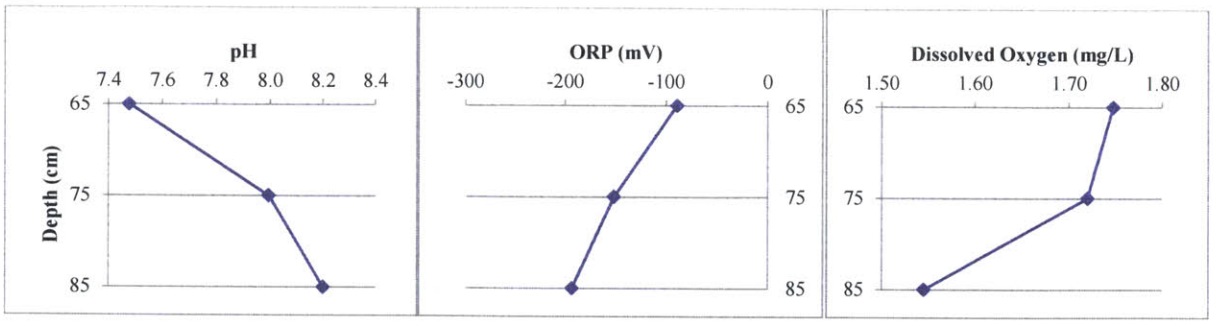

Figure 3: DO, pH, and ORP as a function of vertical profile depth

4.1.2 Nitrogen Parameters

Average concentration values and removal rates as a function of depth are reproduced in Tables 2 and 3. Removal rates in Table 3 are calculated as $(C_1-C_0)/C_0$. Nitrate levels, although initially low at an average of 0.3 mg/L, still decreased by 73% through the anoxic layer (65 to 85 cm) and 88% from the top of the anoxic layer to the pipe outflow. Initial nitrite levels were even lower, averaging 0.05 mg/L, but still decreased 60% from the top of the anoxic layer to the pipe outflow (Tables 2 and 3). In many cases, both of these parameters decreased to the detection limit of the analytical method.

Ammonia concentrations stayed fairly constant through the anoxic layer at about 0.1-0.15 mg/L, and then increased sharply between the bottom of the anoxic layer and the pipe outflow (Figures 4 and 5). Ammonia increased by 50% through the anoxic section, and increased by 290% from the top of the anoxic layer to the pipe outflow (Table 3). One ammonia concentration data point from the southwest section of the garden at 65 cm, an order of magnitude higher than any other ammonia data point, was excluded from analysis based on Dixon's Q Test (Appendix C). More data from the southwest section is necessary for a more rigorous analysis of ammonia profiles.

Table 2: Nitrogen species concentration averages a function of depth

Depth (cm)	Nitrate (mg/L)	Nitrite (mg/L)	Ammonia (mg/L)	TN (mg/L)	TKN (mg/L)
65	0.30	0.05	0.10	1.29	1.12
75	0.07	0.03	0.10	1.45	1.26
85	0.08	0.04	0.15	1.84	1.62
Outflow Pipes	0.03	0.02	0.39	0.65	0.59

Table 3: Average removal rates for nitrogen species. Positive rates (removal) are in black, while negative rates (export) are in red. Total removal rates are bolded for visibility. "Total Anoxic Removal" corresponds to the removal between 65 and 85 cm depth.

Region	Nitrate	Nitrite	Ammonia	TN	TKN
65-75 cm	77%	40%	0%	-12%	-13%
75-85 cm	-14%	-33%	-50%	-27%	-29%
85 cm-outflow pipes	63%	50%	-160%	65%	64%
total removal	**90%**	**60%**	**-290%**	**50%**	**47%**
total anoxic removal	**73%**	**20%**	**-50%**	**-43%**	**-45%**

The Pearson product-moment correlation coefficient between TN and TKN was calculated using Microsoft Excel. TN and TKN are correlated with a correlation coefficient in excess of 0.99 in both vertical profile samples and pipes. Both parameters were initially high relative to other nitrogen species concentrations, with an average concentration at the top of the anoxic layer of 1.2 mg/L (Table 2). Concentrations of both parameters increased through the anoxic layer by approximately 44%, then decreased between the bottom of the anoxic layer and the pipe outflow by approximately 64%, for a total average removal rate of 49% (Table 3, Figure 4.)

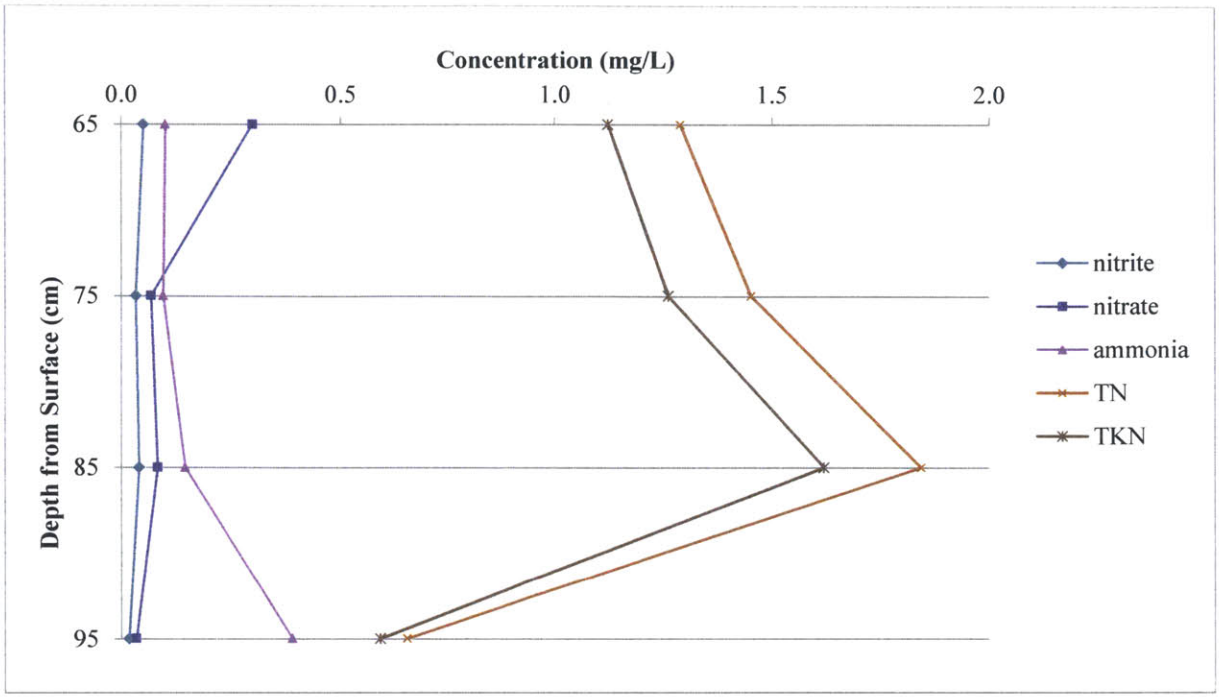

Figure 4: Average nitrogen species concentration (as N) as a function of depth

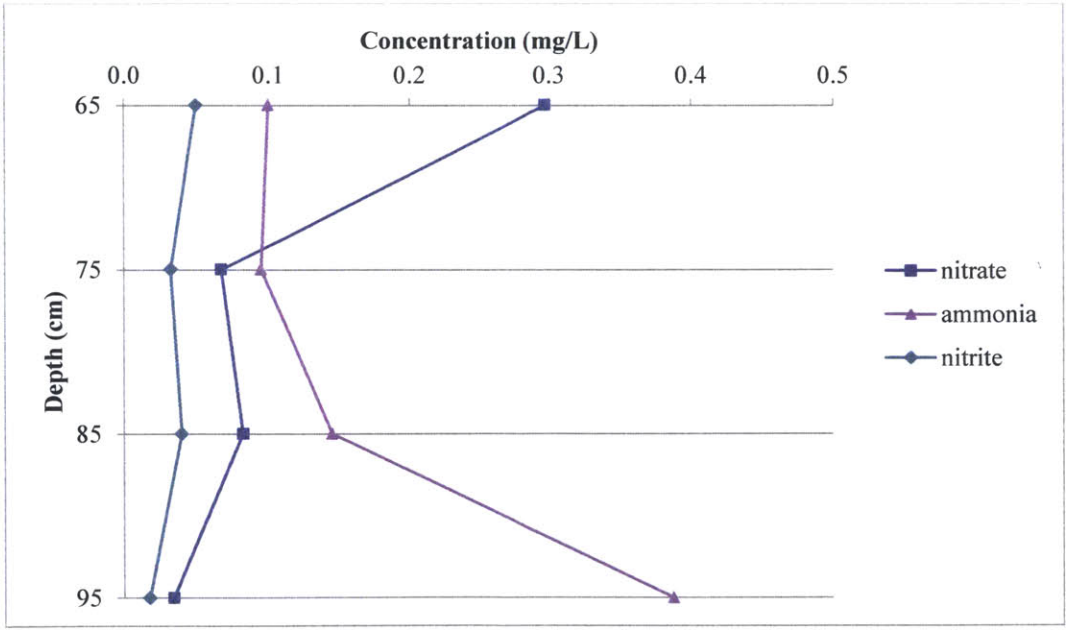

Figure 5: Average inorganic nitrogen species concentration (as N) as a function of depth

4.1.3 Total Organic Carbon and Total Phosphorous

Average TOC and TP concentration values and removal rates as a function of depth are presented in Table 4, with TN data duplicated from Table 2 for comparison. Initial TOC concentrations were high relative to either TN or TP, at an average of 3.0 mg/L. TOC increased over the first ten centimeters of the anoxic zone, then decreased through the remaining distance to the outflow pipes (Table 4, Figure 6); TOC concentrations were correlated with a correlation coefficient of 0.86 with both TN and TKN concentrations (calculated similarly to that in section 4.1.2). TOC removal rates totaled 23% (Table 5). TP started at an average of 0.42 mg/L and decreased consistently from the top of the anoxic layer to the pipe outflows, with an average total removal rate of 64%. This consistent removal indicates that the garden is adequately removing phosphorous from the infiltrating water.

Table 4: TOC, TP, and TN concentrations as a function of depth

Depth from Surface (cm)	TN (mg/L)	TP (mg/L)	TOC (mg/L)
65	1.29	0.42	3.01
75	1.45	0.36	3.49
85	1.84	0.30	2.84
Outflow Pipes	0.65	0.15	2.31

Table 5: TOC, TP, and TN removal rates as a function of depth. Formatting similar to Table 3.

Region	TN	TP	TOC
65-75 cm	-13%	13%	-16%
75-85 cm	-27%	16%	18%
85 cm-outflow pipes	64%	50%	19%
total removal	**49%**	**64%**	**23%**
total anoxic removal	**-43%**	**27%**	**5%**

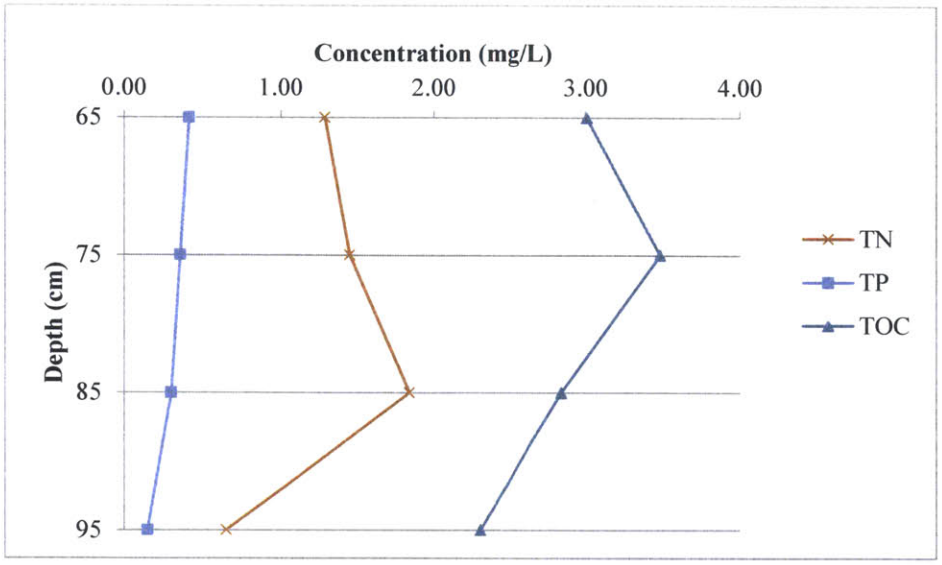

Figure 6: TP, TN, and TOC concentrations as a function of depth

4.2 Differences between Garden Sections

Several parameters of interest exhibited significant differences between the larger, northeast section of the garden and the smaller, southwest section. Qualitatively, all outflow pipes in the southwest section of the garden were drier than all pipes in the northeast section. Similarly, groundwater at 65 cm depth in the southwest section was more difficult to extract. Discussion of quantitative values is necessarily limited, as we were only able to gather one vertical profile in the southwest section. Dissolved oxygen values at all depths in the southwest section were higher than any tested point in the northeast section. TN and TOC were also higher at all points in the southwest section than in the northeast (Figures 7 and 8). Finally, the extremely high ammonia concentration measurement, treated as an outlier, was from the southwest garden section.

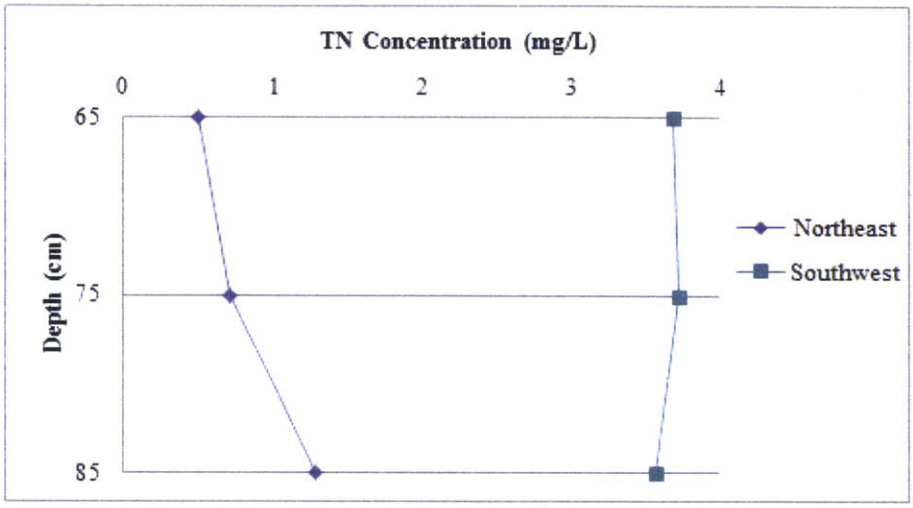

Figure 7: Total nitrogen concentrations (as N) as a function of depth for northeast and southwest sections of the garden

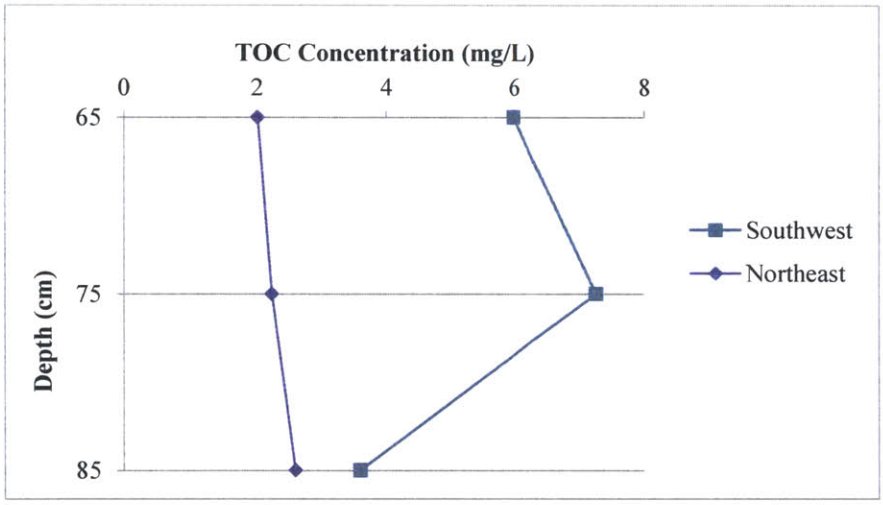

Figure 8: TOC as a function of depth for northeast and southwest sections of the garden

4.3 Elemental Composition Analysis

The soil samples contained three types of material: light tan sand, dark brown "soil-like" material of finer consistency than the sand, and dark brown wood chip pieces. These pieces were a variety of sizes, ranging from approximately 10 mm in length by 1 mm in width down to under 1 mm in length. Upon shaving the wood chip pieces in preparation for CHN analysis, it was

discovered that the larger wood chip pieces exhibit an exterior darkening only, while the interior remains a lighter brown.

As mentioned in Section 3.4, two samples of the darker soil-like material, two samples of dark brown wood chip exterior shavings, and two samples of lighter brown wood chip core shavings were tested. The sand was not tested in the analysis, both as it is assumed to be transition layer material that entered the samples as a result of the augering procedure and because it is presumed to be comprised of mostly silica. No sand was initially present in the anoxic layer at the time of garden construction.

It was found that the soil-like samples had the lowest of all three tested elements, with a carbon content of 10% on average (Table 6, Figure 9). The outer chip samples were significantly higher in carbon content and slightly higher in nitrogen, at 31% and 1.1% on average, respectively. Inner chip samples exhibited significantly higher carbon content, at 45% on average, but very similar nitrogen content, at 1.1% on average. It appears likely that soil-like samples consist of some percentage decomposed wood chip material mixed with sand.

Table 6: Average elemental percentages N, C, and H by sample type

Sample	%N	%C	%H	C:N ratio
"Soil"	0.48	10	2.4	21
Outer Chip	1.05	31	3.8	30
Inner Chip	1.14	45	5.7	40

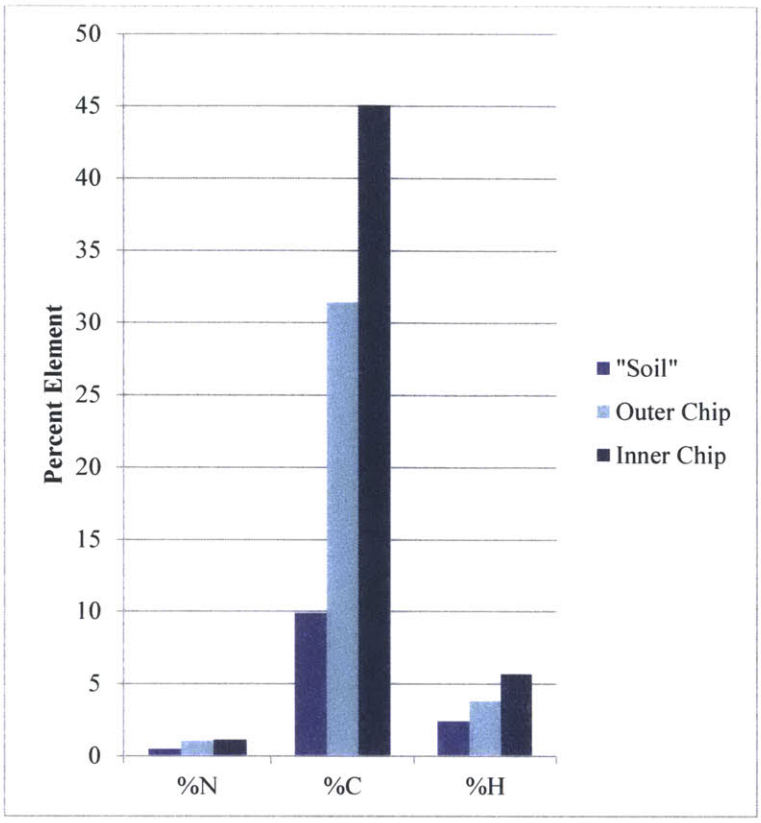

Figure 9: Average elemental percentages N, C, and H by sample type

4.4 Leaching Test

Results of the leaching test described in Section 3.5 show the presence of TN and TKN in the range of 13-23 mg/L, and TOC at approximately 190 mg/L. These results indicate that the anoxic soil layer material is capable of leaching organics.

5. Discussion

5.1 Denitrification

Decreasing nitrate levels with depth indicate that the garden is achieving its design goal of removing nitrate from stormwater (Figure 5). Since conditions in the saturated layer are sufficiently anoxic (Figure 3), it is likely that the nitrate is being removed through denitrification. Dissimulatory nitrogen reduction to ammonia (DNRA) and anoxic ammonium oxidation (anammox) were both considered as potential processes as both occur under anoxic conditions and result in decreased nitrate. However, these processes would cause ammonia concentrations in the 65-75 cm region—the region where the bulk of the nitrate removal occurs—to either increase (in the case of DNRA) or decrease (in the case of anammox). As ammonia concentrations stay constant throughout this region (Figures 4 and 5), these processes are unlikely. Essentially all nitrate removal occurs in the first ten centimeters of the anoxic zone, which suggests that the garden has a larger denitrification potential than is currently being utilized. Literature indicates that this is a common feature of bioretention systems under low nitrate loading levels (Kim et al. 2003).

Anoxic layer material sampling and CHN analysis also suggest that denitrification is occurring. The darker color on the outside of the wood chip pieces as compared with the inside fulfills one qualitative criterion of denitrification presence mentioned in the Saliling et al. study (Saliling et al. 2007), as the inside of the wood chips do not have significant contact with infiltrating water. The presence of darker "soil-like" material, which was not present in quantity when the garden was constructed, is another qualitative indicator of denitrification listed by the Saliling et al. study. The soil-like material, which appears to be a mixture of extremely fine decomposed wood chip and sand, is evidence for decreasing structural integrity of the wood chips. Finally, the observed decrease in the C-to-N ratio between the inside and the outside of the chip (Table 6), specifically as a result of decreasing percentage carbon, is a final indicator of denitrification: the carbon is used during the course of the reaction (Saliling et al. 2007).

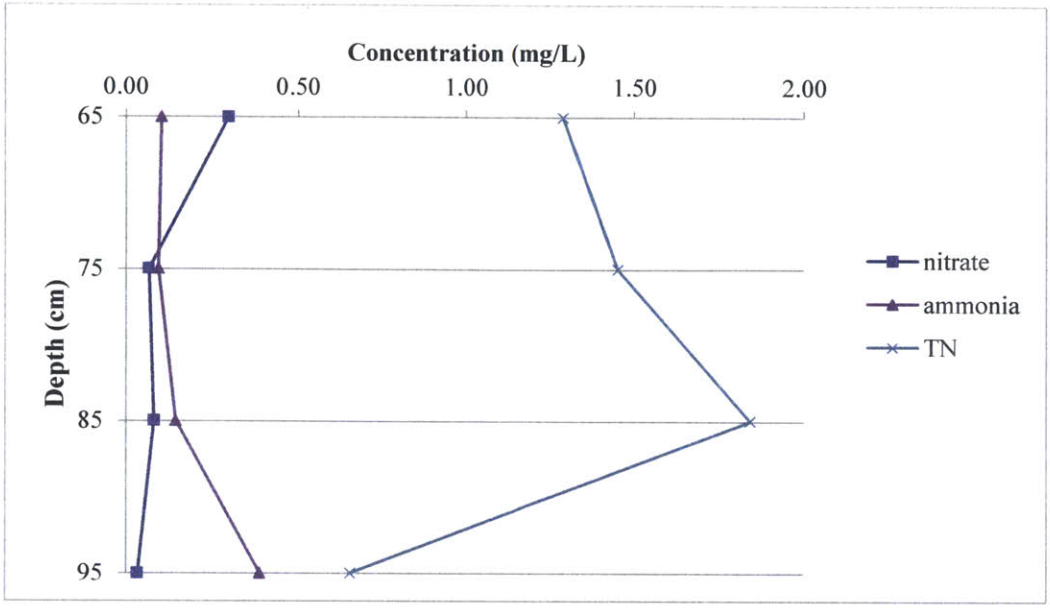

Figure 10: Nitrate, ammonia, and TN concentrations as a function of depth

5.2 TN and TKN

The leaching of organic nitrogen into the water infiltrating through the rain garden is worthy of note, as it can be problematic if conditions allow for mineralization. Increasing TN and TKN concentrations through the anoxic layer of the Balam Rain Garden may be indicative of organic nitrogen leaching from anoxic layer organic material, either from embodied organic nitrogen or organic nitrogen adsorbed from previous storm events. Literature precedent exists for both these phenomena (Palmer 2012; Robertson et al. 2005). Results of the ex-situ leaching test demonstrate that the anoxic layer material is capable of leaching organic nitrogen and carbon, but provides no evidence as to the source of the leached material (i.e. embodied or previously adsorbed). Leaching from embodied organic nitrogen is more problematic than leaching from nitrogen adsorbed from previous storm events, because the former represents a true export of nitrogen not previously contained in the runoff water. This would seriously call into question the efficacy of the garden. However, literature sources indicate that most embodied nitrogen leaching occurs within the first few months of garden operation (Robertson et al. 2005). As the Balam Rain Garden has been operational for over two years, embodied nitrogen leaching may be less likely than adsorption from previous storm events. More data are needed; an in-situ isotope tracer study is suggested as a future line of inquiry.

Although the focus of this research is on the garden's anoxic layer, performance between the bottom of the anoxic layer and the outflow pipes is clearly a relevant factor in rain garden performance. Concentrations measured in outflow pipes suggest that there is air in the pipes, but conditions vary widely. A decrease in TN and TKN accompanied by an increase in ammonia concentrations under aerobic conditions (Figure 10) may indicate problematic mineralization of organic nitrogen species to more bioavailable inorganic nitrogen. The increase in ammonia is not sufficiently large to account for the entire decrease in TKN, and the transformation of the remaining material is unclear. This may be a future avenue of inquiry.

5.3 Differences Between Garden Sections

From the relatively limited data in the smaller southwest section, we can make a few tentative inferences. First, the southwest section of the garden appears to be uniformly drier. Data supporting this conclusion include the higher dissolved oxygen content of both groundwater and outflow pipe samples. Higher DO in groundwater suggests less saturated subsurface conditions, while higher DO in pipe outflows suggests the presence of air in the pipes. Furthermore, qualitative observations directly noted drier conditions upon attempting to pump both groundwater and outflow water in the southwest section. According to the design of the garden, the southwest section drains into the northeast section, which then drains to Pelton Canal. Uneven drainage and storage rates could conceivably cause a difference in saturation between the two garden sections, although this would have to be a future line of inquiry.

The high TN and TOC values in the southwest section likely indicate a higher rate of organic leaching, since the influent water to both sections is identical. More information is required to make confident conclusions as to why this material would be leaching more. However, when viewed with the data on dryness, one hypothesis is that the (wetter) northeast section experiences more complete volumetric turnovers per given unit of time than does the drier southwest section. This would cause any adsorbed or embodied organic material to be more rapidly and consistently flushed through the system in the northeast section, thereby displaying lower concentrations in sampled water. This hypothesis could be tested in future research.

6. Recommendations for Future Work

The most critical recommendation for future work in the Balam Rain Garden is to conduct a nitrogen isotope tracer study to determine the source of the leaching organic nitrogen. This type of study would involve spiking influent stormwater with nitrogen isotopes, and then conducting several samplings of groundwater and outflow water over time to see how the isotopes had partitioned into the various nitrogen compounds. Observing which nitrogen species become isotopic, if any, will illuminate nitrogen transformation pathways in the garden and is likely to address the question of the source of excess organic nitrogen in groundwater. A full analysis of the performance of the garden is not possible until the question of possible organic nitrogen export from the garden is answered.

Additionally, further study of the nitrogen chemistry in the comparatively oxygen-richer pipe outflow area is indicated. Conditions in this area are fluctuating and intermittent, ranging from nearly continuous flow to almost entirely dry, and evolving based on the timescales of storm events. This necessitates more samples over time in order to form a more complete picture of outflow pipe conditions, which will allow for a greater understanding of chemical environments. The potential for problematic organic nitrogen remineralization is a compelling reason to partake in more intensive sampling over. Finally, it would be illuminating to execute a more thorough investigation of the differences between the northeast and southwest sections of the garden. Preliminary data in this study suggests that significant differences in performance may exist; the hypothesis that these performance differences are due to drier conditions in the southwest section is potentially testable.

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Appendix A: Groundwater Sampling Data

profile-depth	Temperature	pH	ORP (mW)	DO (mg/L)	nitrite (mg/L)	nitrate (mg/L)	NH3 (mg/L)	TP (mg/L)	TN (mg/L)	TKN (mg/L)	TOC (mg/L)
1-65 cm	27.8	6.69	73	1.65	0.02	0.83	0.00	0.23	0.33	0.20	2.18
1-75 cm	28.1	7.42	-146	1.99	0.03	0.05	0.17	0.20	0.55	0.48	2.41
1-85 cm	28.1	7.74	-200	1.20	0.03	0.05	0.29	0.14	0.84	0.9	2.93
2-65 cm	28.7	7.73	-95	0.89	0.02	0.06	0.18	0.28	0.43	0.30	1.64
2-75 cm	28.5	7.49	-121	1.44	0.03	0.06	0.06	0.14	0.70	0.58	1.92
2-85 cm	28.6	8.06	-182	1.50	0.05	0.13	0.08	0.17	2.03	1.55	2.50
3-65 cm	28.4	7.65	-179	1.47	0.04	0.12	0.13	0.32	0.72	0.70	2.22
3-75 cm	28.9	8.52	-161	1.69	0.04	0.06	0.03	0.39	0.84	0.83	2.35
3-85 cm	28.7	8.30	-217	1.27	0.03	0.05	0.15	0.45	0.93	0.89	2.34
4-65 cm	29.4	7.84	-154	2.98	0.12	0.18	**2.04**	0.83	3.68	3.29	5.99
4-75 cm	28.9	8.55	-178	1.76	0.03	0.10	0.12	0.71	3.72	3.16	7.26
4-85 cm	28.5	8.70	-174	2.21	0.05	0.10	0.06	0.45	3.57	3.14	3.60

Appendix B: Outflow Pipe Water Sampling Data

	which side?	dryness	DO (mg/L)	nitrite (mg/L)	nitrate (mg/L)	NH3 (mg/L)	TP (mg/L)	TN (mg/L)	TKN (mg/L)	TOC (mg/L)
Pipe 1	NE	normal	5.40	0.05	0.09	1.03	0.14	1.97	1.87	2.95
Pipe 2	NE	wet	2.11	0.01	0.01	0.18	0.13	0.36	0.34	2.98
Pipe 3	NE	dry	7.01	0.06	0.10	0.23	0.25	0.53	0.49	2.36
Pipe 4	NE	wet	2.83	0.01	0.01	0.18	0.16	0.40	0.40	1.58
Pipe 5	NE	wet	2.41	0.01	0.02	0.23	0.07	0.32	0.30	1.68
Pipe 6	SW	normal	4.83	0.01	0.02	0.29	0.12	0.41	0.38	1.70
Pipe 7	SW	dry	5.49	0.01	0.02	0.48	0.19	0.67	0.53	2.26
Pipe 8	SW	normal	3.79	0.00	0.02	0.40	0.18	0.64	0.55	3.15
Pipe 9	SW	normal	3.13	0.00	0.02	0.47	0.12	0.59	0.47	2.12

Appendix C: Outlier Analysis for Ammonia Data

Dixon's Q test (Dean and Dixon 1951) was used to determine whether the highest data point was likely to be an outlier. This test calculates the Q-value specified in Equation 2 for a given data set, and compares it to tabulated critical Q-values for various numbers of observations. If the calculated Q is greater than the critical Q, the data point can be set aside as an outlier.

$$Q = \frac{\text{gap}}{\text{range}} \tag{2}$$

The groundwater ammonia data were as follows, ordered from smallest to largest:

Table 7: Groundwater ammonia concentrations in mg/L

0
0.03
0.06
0.06
0.08
0.12
0.13
0.15
0.17
0.18
0.29
2.04

The calculated value of Q for the 2.04 mg/L data point was 0.86. The critical value of Q for 12 data points is 0.52 at the 99% confidence level. Since the calculated value is greater than the critical value, the data point is highly likely to be an outlier.

Appendix D: CHN Analysis Data

Sample	Mass (mg)	%N	%C	%H	Daily N factor	Daily C factor	Daily H factor
Dirt 1	17.04	0.27	5.41	2.85	0.94	0.83	0.93
Dirt 2	5.70	0.69	14.35	1.97			
Avg Dirt		**0.48**	**9.88**	**2.41**			
Outer Chip 1	2.52	1.17	35.25	4.24			
Outer Chip 2	2.61	0.94	27.61	3.37			
Avg Out Chip		**1.05**	**31.43**	**3.81**			
Inner Chip 1	6.52	1.12	44.90	5.65	0.96	0.95	0.95
Inner Chip 2	4.89	1.16	45.23	5.70			
Avg In Chip		**1.14**	**45.07**	**5.67**			